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MAPPING OF THE ENERGY LEVELS OF METALLOPHthalocyanINES VIA ELEC--ETC(U)

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MAPPING OF THE ENERGY LEVELS OF METALLOPHthalocyanines VIA  
ELECTRONIC SPECTROSCOPY, ELECTROCHEMISTRY, AND PHOTOCHEMISTRY

BY

A.B.P. Lever<sup>\*</sup>, S. Licoccia, K. Magnell, P.C. Minor and B.S. Ramaswamy

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# Mapping of the Energy Levels of Metallophthalocyanines via Electronic Spectroscopy, Electrochemistry, and Photochemistry

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*The mapping of the energy levels in metallophthalocyanines is accomplished by a combination of electrochemistry, electronic spectroscopy, and photochemistry. This chapter reviews the electrochemical properties of metallophthalocyanines and includes a large amount of previously unpublished data. The results are rationalized in terms of the nature of the electron transfer, that is, redox at metal or ligand. Well-defined correlations are shown to exist between the ease of oxidation or reduction of the phthalocyanine ligand and the oxidation state, and/or polarizing power, of the metal ion. Solvent and ring substitution effects also are presented and explained. Charge transfer transition energies can be calculated directly from these data, and agreement between experiment and theory is excellent. Finally, the data are used to calculate both the photo-generated excited state redox energies and the thermodynamics of quenching by donors and acceptors.*

**P**hthalocyanine (MPc) complexes have significant importance for many reasons, including their similarity to the biologically important metalloporphyrins, their classical use as dyestuffs, and their developing use as components of various solar energy conversion devices.

Of paramount importance in understanding and predicting the physics and chemistry of the metallophthalocyanines is knowledge of the energy levels therein. This knowledge can be gained through study of the electronic spectroscopy (absorption and emission), electrochemistry, photochemistry (and photophysics), and photoelectron spectroscopy of these species. In this chapter we address the first three of these techniques and consider the information obtained from their use.

The lower excited states (up to at least  $35,000\text{ cm}^{-1}$ ) of a wide range of metallophthalocyanine derivatives can be identified and mapped. These states vary as a function of the environment (solvent, axial coordination, etc.), phthalocyanine ring substituent, nature and size of metal ion, oxidation state, and electronic configuration.

The excited states may be classified as  $\pi-\pi^*$  and  $n-\pi^*$  transitions, primarily located on the phthalocyanine ring. The ligand (Pc ring) to metal charge transfer (LMCT), metal to ligand charge transfer (MLCT), and  $d-d$  transitions primarily occur on the metal atom. These transitions may occur in two spin manifestations. In addition, spin coupling can occur between metal ion ground state wave functions and excited state wave functions of the phthalocyanine ring to yield a range of triplet-multiplets.

The following three sections review progress in the electrochemistry, electronic spectroscopy, and photochemistry of metallophthalocyanines. The data reported for metallophthalocyanines may be compared usefully with the data obtained for the porphyrins discussed in Chapter XX in this volume.

### Electrochemistry

Many reports (1-18) discuss the electrochemical properties of the metallophthalocyanines, but only in recent literature have these data coalesced into a useful working body of knowledge.

In general, oxidation and reduction are expected at the metal center and at the phthalocyanine ring. In each case, one or more electron transfer processes may be observed. Indeed, two successive ring oxidations and up to four successive ring reductions may occur. Ring reductions are generally electrochemically reversible, but ring oxidations usually are not (at least on platinum). Generally, no more than two redox processes were characterized at a given metal center.

Identification of the nature of a given redox product usually is based on electronic spectroscopy and, where relevant, electron spin resonance (ESR) spectroscopy (2,9,12). Generally, it is possible to deduce unequivocally whether a reduction or oxidation occurred at the metal center or phthalocyanine ring. Phthalocyanine anion and cation radical electronic spectra are quite distinct from those of the  $Pc(-2)$  species, (12,19) although some confusion may exist when low-oxidation state transition-metal ions, such as iron(I), are involved (9).

The higher filled and lower empty energy levels of a typical metallophthalocyanine are illustrated in Figure 1 (20-23). The two highest filled orbitals of relevance to our discussion are  $\pi$  orbitals with  $a_{1u}$  [highest occupied molecular orbital (HOMO)] and  $a_{2u}$  symmetry, respectively; and the lowest empty ring orbitals are the  $e_g$  [lowest unoccupied molecular orbital (LUMO)] and  $b_{2u}$   $\pi^*$ -orbitals. The metal valence orbitals may be buried inside the filled phthalocyanine levels, or filled and/or empty valence orbitals may occur in the HOMO-LUMO gap; in addition, empty metal orbitals may lie at energies comparable to, or above, the LUMO phthalocyanine level.

Phthalocyanine redox chemistry may be classified conveniently into two sections: main groups and transition groups.

**Main Group Phthalocyanine Electrochemistry.** Redox chemistry in the main groups is usually quite straightforward; generally the metal atom center is unaffected, and all observable processes occur on the phthalocyanine ring. For main group ions that lie in the phthalocyanine plane, the first ring oxidation (from HOMO) is separated from the first ring reduction (to LUMO) by approximately 1560 mV (Table I), which is the magnitude of the molecular bandgap. This value seems largely unaffected by the nature of the main group metal, although some deviation may occur if the metal is too large to be accommodated by the phthalocyanine center (14).

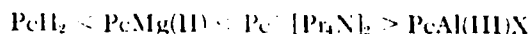
However, the absolute energies of first oxidation or reduction vary considerably, and depend on the size and charge of the metal ion. The ease of oxidation or reduction of the phthalocyanine unit depends on the electric field generated by the central metal ion. Indeed, there is a clear relationship between the polarizing power of the central ion, expressed as  $(ze/r)$  and the redox energy. The more polarizing is the ion, the easier it is to reduce the phthalocyanine ring, and the more difficult the ring is to oxidize. A good linear relationship is observed between these quantities (14) defined by Equations 1 and 2:

$$\text{oxidation } (ze/r)(E^0 - 1.410) = -0.012 \quad (1)$$

$$\text{reduction } (ze/r)(E^0 + 0.145) = -0.012 \quad (2)$$

where the potentials are referenced to NHE and the radii used originate from Shannon and Prewitt (24). The lines are essentially parallel. These data imply a HOMO-LUMO separation of about 1.56 V independent of the central main group ion, provided it lies in the plane (14). This treatment is discussed later.

The second reduction process appears, on the average, about 420 mV more negative than the first reduction (Table I) but these potentials are more scattered and less directly dependent on the polarizing power of the central ion; nevertheless, metallophthalocyanines with the more polarizing ions are generally more readily reduced to the ring dianion. The third- and fourth-reduction processes occur near -1.7 to -1.8 and -2.0 V (Table I) (12) (for both main and transition group ions). These data are displayed in Figure 2. For the first two reduction processes, the ease of reduction follows the sequence:



This sequence may be rationalized in terms of increasing negative charge on the phthalocyanine ligand when passing from the covalent NH bond in  $\text{PcH}_2$ , to a fairly electrostatic interaction with the electropositive magnesium, and finally to a full negative charge with the propylammonium salt. For aluminum(III), the high polarizing power of this ion leads to a more covalent interaction and a reduced negative charge on the phthalocyanine ligand. These potentials monitor the negative charge on the phthalocyanine ligand.

**Transition Group Phthalocyanine Electrochemistry.** The presence of a transition metal ion appears to perturb the redox processes occurring at the phthalocyanine unit; however, a pattern similar to the main group species can be discerned. In many cases, one or more redox processes may occur at the central ion at potentials lying between ring oxidation and reduction. If the solvent, supporting electrolyte, or an added ligand can bind to the axial sites of the metal ion in one (or more) of its oxidation levels, then the observed redox potential often depends markedly on the choice of solvent, electrolyte, or added ligand.

Table II gives data for transition metal ion phthalocyanines where solvent coordination is not strongly perturbing, that is, in weak donor solvents, or involving metals that bind weakly along the axis. These data should be generally interpretable without taking into consideration severe perturbation by solvent effects.



Electronic and ESR spectroscopy demonstrated that the OTi(IV), OV(IV), Ni(II), Cu(II), and Zn(II) species do not undergo redox processes at the metal at potentials between ligand oxidation and reduction. Iron and cobalt, on the other hand, can form M(I), M(II), and M(III) species at these intermediate potentials, that is, oxidation of the phthalocyanine ligand occurred after the metal was oxidized to M(III), and reduction of the phthalocyanine ligand occurred only after reduction of the metal to M(I). Chromium and manganese phthalocyanines form M(II) and M(III) oxidation states (5-13).

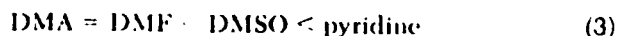
In parallel with main group phthalocyanine chemistry, the ability to reduce a metalophthalocyanine increases, that is, the potential becomes more positive, as the oxidation state of the central ion increases. This ability can be seen from the data comparisons abstracted from Table II and shown in Tables III, IV, and Figure 2.

Not surprisingly, the potentials are similar to those of main group ions of the same oxidation state and approximate size, although this fact apparently was not recognised clearly in the past. Because the spread in potentials for a given metal oxidation state is remarkably small, and there is a clear enough separation between the ranges for at least the first and second reduction, the potentials generally can be used diagnostically to identify the oxidation state of the central transition metal ion.

Most oxidations of the phthalocyanine ring in transition metal phthalocyanines are electrochemically irreversible, obscuring oxidation state trends. Trivalent and tetravalent transition metal phthalocyanines generally oxidize a little above 1.0 V; this trend is also true for the more polarizing divalent ions, nickel(II) and copper(II).  $\text{Pc}(-2)\text{Zn}$  also oxidizes near 1.0 V while the earlier first row transition metal phthalocyanines oxidize at slightly more negative potentials.

Solvent effects on these ligand redox potentials are small. However, solvent effects on metal redox process potentials can be extraordinarily large. Table V gives the ranges for various redox processes as a function of solvent and/or supporting electrolyte. The effect of solvent depends clearly on the electronic configurations of the species involved, and the effect of supporting electrolyte depends on whether there is binding of the anion to either component of the couple.

The iron(II)/iron(I) and cobalt(III)/cobalt(II) couples both involve low spin  $d^6/d^7$  configurations. Strongly binding axial ligands (solvent molecules) destabilize the  $z^2$  electron (in  $d^7$ ) and favor oxidation to the low spin  $d^6$  species. Thus, in both cases the potentials shift negatively with increasing donor strength of the solvent, which follows the order



where DMA, DMF, and DMSO represent dimethylamine, dimethylformamide, and dimethyl sulfoxide, respectively.

Indeed, there is a linear correlation of these potentials with Gutmann Donicity Number (25) of the solvent (8). The cobalt(II)/cobalt(I) couple (low spin  $d^7/d^8$ ) also shifts negatively with increasing donicity of the solvent, probably because axial binding to the square planar  $d^8$  cobalt(I) is weak or nonexistent. The iron(III)/iron(II) couple (low spin  $d^5/d^6$ ) however, shows the opposite trend shifting positively with increasing donicity of the solvent (8, 9). This fact best can be explained by synergism, where strongly coordinating axial ligands favor back donation by the low spin  $d^6$  ion into phthalocyanine  $\pi$ -acceptor orbitals. Back donation in iron(III) is weaker because of the greater charge on the metal. Table V shows that these solvent effects can be quite dramatic. For example, a solution of iron(II) phthalocyanine in pyridine containing chloride ion is air stable, but a similar solution in DMA or DMF with chloride ion rapidly air oxidizes to iron(III) phthalocyanine.

Moreover, if cyanide ion is added to a solution of tetrasulfonated iron(II) phthalocyanine, the iron(II) state is stabilized to a remarkable degree (Table V) through axial coordination of cyanide ions. Indeed, unsubstituted iron(II) phthalocyanine is soluble in water if cyanide ions are present (5). Even more remarkable stabilization of iron(II) is seen when imidazole is used as an axial ligand (Table V) (7).

When a series of substituted pyridines were used as solvents (8), both the cobalt(III)/cobalt(II) and cobalt(II)/cobalt(I) couples shifted negatively with increasing  $pK_a$  of the solvent. This result may be explained in terms of the Drago E and C model (26) given that for this series the electrostatic component, E, is changing while the covalent component, C, remains roughly constant, an observation in agreement with similar porphyrin redox data (27). An interesting solvent effect is observed when cobalt(II) Pc is oxidized to cobalt(III) Pc. Because the latter species has a very strong propensity to be hexacoordinated with two axially bound solvent molecules, the oxidation potential is clearly solvent dependent. In a noncoordinating solvent such as dichlorobenzene, a hexacoordinated cobalt(III) species cannot be formed. Under these conditions, the Co(III) Pc/Co(II) Pc couple shifts positively to a considerable extent, such that the initial oxidation of the species is to form a cobalt(II) phthalocyanine cation radical (16). When pyridine is added to such a solution, a cobalt(III) species apparently is formed.

Preliminary data for chromium(III) phthalocyanines reveal increased stabilization of chromium(II) with strong donor solvents. This effect could be due to stabilization of the low spin  $d^4$  chromium(II) through back donation to the phthalocyanine ring. However, further data are necessary to understand this phenomenon, especially as a similar stabilization of low-spin  $d^5$  manganese(II) phthalocyanine apparently is not evident (Table V). Some data exist concerning the effect of ring substitution on redox energies (see Table II); however, significantly less so than in the porphyrin series (28). Generally, electron donors favor ring oxidation and disfavor ring reduction. An interesting comparison exists for sulfonic acid substitution where the neutral acid form of TsPcFe(III) reduces at  $-0.40$  V [vs. normal hydrogen electrode (NHE)] while the sodium salt, with four negative charges on the periphery of the molecule, does not reduce until  $-0.67$  V (5). The second reduction is similarly, but a little less markedly, effected. For substituents such as chloride, methyl, *tert*butyl, sulfonic acid, carboxylic acid, and others, the shifts in redox energies (except for special cases such as just indicated where the charge on the ring is modified) rarely exceed 100 mV.

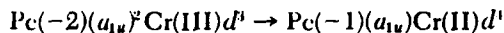
#### Electronic Spectroscopy

Gouterman et al. (20)<sup>27</sup> first detailed the electronic structure of metallophthalocyanines, showing that the two principal bands (both  ${}^1E_u \leftarrow {}^1A_{1g}$ ) (for  $S = 0$  metal ions) in the visible spectrum of all phthalocyanine ( $-2$ ) species could be assigned as  $a_{1u}(\pi) \rightarrow e_g(\pi^*)$  ( $Q$  band near 600 nm) and  $a_{2u}(\pi) \rightarrow e_g(\pi^*)$  (Soret band near 350 nm). Unlike the porphyrin system (28), the  $a_{1u}$  and  $a_{2u}$  orbitals are fairly well-separated in energy, and these two transitions do not, therefore, mix appreciably. Emission data reveal that the spin triplet component of the  $Q$  band lies about  $5000\text{--}5500\text{ cm}^{-1}$  below the spin singlet (29). In systems lacking charge transfer absorption, such as most of the main group species, it is this spin triplet state that is likely to be photoactive when the phthalocyanine is utilized as a photocatalyst. The  ${}^1Q$  state (fluorescence) has a lifetime of only a few nanoseconds, while the triplet state lifetime is in the microsecond-millisecond region at liquid nitrogen temperature (29, 30). Where paramagnetic ions such as copper(II) are concerned, this lowest state most likely is a triplet-multiplet, lying at roughly the same energy as  ${}^3Q$  (28, 31).

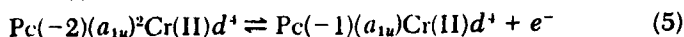
However, the situation can change dramatically when charge transfer transitions are present. Such transitions occur whenever metal *d*-levels lie at energies inside the HOMO-LUMO bandgap of the phthalocyanine (or close to, but above the LUMO energy). Such transitions were discussed in depth (31) and only a summary of these data is provided here.

With moderately oxidizing ions such as manganese(III) and chromium(III), charge transfer absorption from both the phthalocyanine  $a_{1u}$  and  $a_{2u}$  orbitals into  $eg(d)$  orbitals on the metal is allowed electronically and observed readily, the former transition lying in the near IR region (Figure 1, Table VI).

Consider the charge transfer transition:



labeled LMCT1 in Figure 1. This reaction may be construed as the sum of two redox processes, viz:



whose potentials<sup>2</sup> [-0.40 and -(+0.70)V] can be summed to yield a transition energy of 1.10 eV, that is, a predicted charge transfer energy of 8870  $cm^{-1}$ , in satisfactory agreement with an observed transition at 7900  $cm^{-1}$ . Both chromium(III) and manganese(III) exhibit charge transfer bands in the near IR region, although for manganese(II) and chromium(II) species these LMCT bands are blue-shifted to approximately 11,000  $cm^{-1}$ . A treatment similar to the one indicated in Equations 3-5 allows prediction of the energies of these charge transfer transitions generally to within an accuracy of about 1000  $cm^{-1}$  (Table VI).

Further proof of the assignment is obtained by location of a second charge transfer band (LMCT2), arising from  $a_{2u}$  to  $eg(d)$  (Figure 1), lying between the Q and Soret bands. Most significantly, the energy separation between these two charge transfer bands is almost exactly equal to the energy separation between the Q and Soret bands (31). Virtually all the anticipated LMCT bands in the first-row transition metal phthalocyanines can be assigned and calculated by this simple procedure. LMCT band energies also can be calculated, but appear to be too weak to be observed. The energies of orbitally forbidden LMCT transitions also can be derived by this technique, allowing the presumed detection of states that cannot be observed directly by electronic spectroscopy (see Table VI).

Surprisingly, such a simple relationship between electronic absorption bands and redox potential energies is successful. Evidently, the entropy differences between the various components of the couple are very small. Moreover, the LMCT transitions appear to be (0-0) in vibrational character, eliminating another possible source of disagreement between calculated redox energy and observed data (31). Precedent for such agreement between charge transfer energies and sums of redox potentials exists (32, 33). Because these LMCT transitions frequently lie at energies below the Q band, they (or higher spin versions) are likely to be photochemically active. However, lifetime data are not yet available.

Hence, a combination of electronic absorption spectroscopy and electrochemical measurement can map the energy levels of a metal-phthalocyanine with considerable accuracy, and provide a measure of the redox potentials of the various excited states, information of considerable value in understanding photochemical behavior. Although few heavy transition metal ion phthalocyanines have been investigated to date, their behavior is not expected to vary greatly from the details presented in this chapter (provided the metals lie inside the phthalocyanine macrocycle ring). In general, their *d*-levels will be buried below the phthalocyanine HOMO level and redox processes at the metal are not expected.

### Photochemistry

A range of main group, first row, and later transition metal ions were screened recently for their ability to generate reduced methyl viologen ( $MV^+$ ) when irradiated (into the  $Q$  band) in the presence of methyl viologen ( $MV^{2+}$ ) and a donor such as triethanolamine (34). Species containing Mg, TiO, Cr(II), Fe(II), Zn(II), Rh(III), and Ru(II) generated reduced methyl viologen, albeit in small yield (<.01%). Other metal ions, specifically VO, Cr(III), Mn(III), Fe(III), Co(II), Ni(II), and Cu(II) did not generate reduced methyl viologen under similar conditions.

Ions with low lying (near IR) LMCT bands clearly were photochemically inactive because much of the excitation energy was lost by intersystem crossing from the  $Q$  band to the low lying LMCT band.

Several mechanisms are possible by which reduced methyl viologen ( $MV$ ) might be produced. Specifically, reductive quenching of the excited state of the photocatalyst ( $c^*$ ) by the donor, yielding  $c^-$ , could result in formation of  $MV^+$  by reaction of  $MV^{2+}$  with  $c^-$  in a following thermal reaction. Alternatively,  $c^*$  could be quenched oxidatively by  $MV^{2+}$  yielding  $MV^+$  directly, together with  $c^+$ , which could then return to the ground state  $c$  by a thermal reaction with the donor.

Detailed kinetic studies, not yet undertaken, are necessary to deduce unequivocally which mechanism is occurring.

Given the ground state redox data discussed in the section on electrochemistry, together with the electronic absorption data given in the section on electronic spectroscopy, the redox potentials of the excited states,  $c^*$ , can be derived (35-37). Thus, if  $E_{en}$  (in electron volts) is the equilibrated excited state energy of the lowest, photochemically active, excited state of the photocatalyst, then the redox potentials involving  $c^*$  are:

$$c^+/c^* = c^+/c - E_{en} \quad (6)$$

$$c^*/c = c^-/c + E_{en} \quad (7)$$

These equations should be fairly accurate provided that the entropy differences between ground and excited states are small, as apparently is the case.

With these data, it is clearly possible to calculate the thermodynamic driving forces for the various excited state and ground state reactions, discussed above. When this is carried out [34] the complexes are readily divided into two sets, one in which the thermodynamics of one or more processes make most unfavourable the production of reduced methylviologen and one in which the thermodynamics are less unfavourable or even slightly favourable. Experimentally the inactive metallophthalocyanines clearly belong to the former set, and the active species to the latter set. In no case, however, studied so far, are the thermodynamics for the formation of reduced methylviologen strongly favourable explaining, in part, why the yields have not been high for these species.

Kinetic phenomena, that is, suppression of otherwise thermodynamically favourable back reactions, play a dominant role in determining which catalysts are suitable and which are not. It is equally clear from this investigation [34] that studies such as those shown in the "electrochemistry" and "electronic spectroscopy" can provide a sound basis for understanding photocatalytic behaviour and can influence the design of future catalysts. Growing interest in the use of metallophthalocyanines in solar energy conversion attests to the potential value of such catalysts (2,15, 34,38-43). Such data are also of significant value in understanding biological photoredox behaviour, especially events occurring during photosynthesis.

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<sup>1</sup> The phthalocyanine nomenclature used here is presented in Ref. 19.

<sup>2</sup> An energy level of symmetry ( $x_2$ ) localized on the peripheral nitrogen atoms is omitted because there is no evidence that it plays a role in the spectroscopy.

<sup>3</sup> Estimated potential is given in Ref. 31.

Table I. Main Group Metallophthalocyanine Electrochemistry

Complex	Solvent <sup>b</sup>	$E^{\circ}/V$ <sup>c</sup>	$E^{\circ}/V$	$E^{\circ}/V$	$E^{\circ}/V$	$E^{\circ}/V$	$E^{\circ}/V$	$E^{\circ}/V$	Reference
PcSi(IV)R <sup>a</sup> PcAl(III)Cl	DMF			-0.30	-0.895				14
	DMA		1.39	-0.26					16
	DMF			-0.29	-0.74	-1.18	-1.74		12
	DMF		1.155	-0.415					tw <sup>c</sup> , 14
	DMF		1.18	-0.415	-0.86				6
PcGa(III)Cl PcIn(III)Cl	DMF		1.15	-0.42					15
	DMF		1.105	-0.495	-0.895				tw, 14
	DMF		1.070	-0.475	-0.710				14
	DMF		1.080	-0.41					15
	DMF		0.94	-0.71					16
PcMg(II)	DMF			-0.67	-1.15	-1.90	-2.34		12
	DMF		1.50	-0.68	-1.04				tw, 14
	DMF		1.50	-0.725					6
	DMA		0.85	-0.72					15
	DMF			-0.93					tw, 6, 14
PcCd(II) PcHg(II)	DMF		0.78	-1.06					14
	DMF		0.49	-1.06					tw
	DMF		0.490	-1.065	-0.770				9, 14, 15
	DMF		0.91	-0.48	-0.840				tw
	DMF	1.01	0.695	-0.250					15
PcBa(II) PcNa(I) Pc <sup>+</sup> (PRA) <sup>z</sup> PcH <sub>3</sub>	DMF			-0.82					12
	CIN		1.34	-1.00	-1.31	-1.71	-1.95		10
	DMF		0.865	-0.58					15
	DMF			-0.42	-0.82	-1.69	-1.99		12
	DMF			-0.58	-0.95				44
TbPcH <sub>3</sub> TSPcH <sub>3</sub>	CHC	1.18	0.865	-0.58	-0.73	-1.57			11
	DMSO		1.14 <sup>e</sup>	-0.285					

Note: Data rounded off to 5 mV. Redox potentials,  $E_{ox}$ , vs. NHE.

<sup>a</sup> R = *O*-*i*-Amyl.

<sup>b</sup> Solvents: DMF, dimethylformamide; DMA, dimethylacetamide; DMSO, dimethyl sulfoxide; CIN, chloronaphthalene; CHC, dichloromethane; tw, this work.

<sup>c</sup> PRA, *N*-propylammonium cation.

<sup>z</sup> two-electron oxidation.

$\frac{1}{2} \text{Fe}(\text{II})$

-0.56 -0.91

45

Table II. Transition Metal Phthalocyanine Redox Potentials in Weakly Coordinating Solvents vs. NHE

Complex	Electronic spectrum		$c^{+/c^+}$	$c^+/c$	$c/c^-$	$c^-/c^-$	Reference
	$\lambda$ Band	Soret					
TbPcTi(IV)O	14.43	28.33		1.09	-0.275	-0.780	tw
TbPcV(IV)O	14.31	29.00		1.18	-0.335	-0.840	tw
TbPcCr(II)	14.82	28.74		0.945	-0.630	-1.115	tw
TsPcCr(III)Na <sub>3</sub>	14.37	28.09		0.75?	-0.155	-0.760	tw
TbPcMo(III)OAc	13.97	27.17		<u>0.100</u>	<u>-0.125</u>	-0.650	tw
PcMn(II)	15.15			<u>0.84</u>	<u>-0.450</u>		3
TdPcFe(II)	14.81	27.93		<u>0.615<sup>a</sup></u>	-0.310 <sup>a</sup>	-0.93 <sup>a</sup>	tw
PcFe(II)				-0.130	-1.160 <sup>a</sup>		10
PcCo(II)	14.88 <sup>b</sup>	28.74 <sup>b</sup>	1.04 <sup>a</sup>	<u>0.04<sup>a</sup></u>			16
TsPcCo(II)			1.08 <sup>a</sup>	0.64 <sup>d</sup>	0.005	-1.05	tw
TbPcCo(II)			1.40 <sup>c</sup>	0.88 <sup>a</sup>			16
PcNi(II)	14.90 <sup>b</sup>	28.49 <sup>b</sup>		1.29 <sup>b</sup>	-0.61 <sup>b</sup>	-0.99 <sup>b</sup>	10
TsPcNi(II)				1.19	-0.465	-0.90	tw, 18
PcCu(II)	14.75 <sup>b</sup>	28.57 <sup>b</sup>		1.22 <sup>b</sup>	-0.600 <sup>b</sup>	-0.94	10
TbPcCu(II)					-0.675	-1.10	tw
TsPcCu(II)				1.13	-0.510	-0.90	tw
TsPcCu(II)				1.11 <sup>c</sup>	-0.495	-0.875	11
PcZn(II)	14.68 <sup>b</sup>			0.92 <sup>b</sup>	-0.65	-1.09	9, 10
PcZn(II)				1.02	-0.56		16
PcBu(II)C(O)Py	15.70 <sup>f</sup>	29.24 <sup>f</sup>		1.15 <sup>f</sup>			13
PcBu(II)(Py) <sub>2</sub>	16.10 <sup>f</sup>	31.75 <sup>f</sup>		1.01 <sup>f</sup>			13

Note: All data are reported in DMF with TEAP or similar perchlorate supporting electrolyte except those annotated as follows. The letter c represents the complex listed in the left column. Underlined data represent metal oxidation or reduction, otherwise the phthalocyanine is oxidized or reduced. It does not follow therefore that each column represents the same oxidation state for each complex. TbPc, TsPc, and TdPc refer, respectively, to tetra-*t*-butyl-, tetrasulfonyl-, and tetradecylsulfonamidophthalocyanines.

<sup>a</sup> Dimethylacetamide solution.  
<sup>b</sup> Chloromethane solution.  
<sup>c</sup> Two-electron oxidation.  
<sup>d</sup> Irreversible.  
<sup>e</sup> Dichlorobenzene solution.  
<sup>f</sup> Dichloromethane solution.



Table III. Potentials, vs. NHE, for the First Reduction of the Phthalocyanine Ring as a Function of Central Ion Oxidation State

Complex	$Pd(-2)M(IV)O/Pd(-3)M(IV)O$	$Pd(-2)M(II)/Pd(-3)M(II)$	$Pd(-2)M(I)/Pd(-3)M(I)$
TbPcVO	-0.275		
TbPcTiO	-0.335		
TbPcCr		-0.630	
TsPcCr		-0.760	
TbPcMn		-0.650	
TsPcMn		-0.475	
PcMn		-0.450	
PcFe			-0.930
TsPcFe			-0.840
PcCo			-1.16
TsPcCo			-1.050
PcNi			
TbPcCu			
PcCu			
$\bar{f}_2$ Zn		-0.650	

Note: see Table II for references to the literature and abbreviations. In general, the potentials show little solvent dependence.

Table IV. Second Reduction Process for Transition Metallophthalocyanines

Complex	$Pd(-3)M(IV)O/Pd(-4)M(IV)O$	$Pd(-3)M(II)/Pd(-4)M(II)$	$Pd(-3)M(I)/Pd(-4)M(I)$	Ref.
TbPcTiO	-0.780			tw
TbPcVO	-0.840			tw
TbPcCr(II)		-1.115		tw
PcMn(II)		-1.22		3
		-1.26		12
TsPcMn(II)		-1.115		tw
TsPcFe(II)			-1.27	tw
PcFe(II)			-1.32	12
PcCo(II)			-1.56	12
PcNi(II)		-0.99		12
TsPcNi(II)		-0.925 (-1.69)		11
		-0.89		tw
PcCu(II)		-0.94		12
TsPcCu(II)		-0.870 (-1.655)		11
TbPcCu(II)		-1.10		tw
PcZn(II)		-1.09		12
		(-1.82, -2.44)		

Note: See Tables I-III for abbreviations. Bracketed data refer to successive reductions. Redox potentials vs. NHE.

Table V. Solvent Effects on Transition Metallophthalocyanine/Redox Potentials vs. NHE

Metal Ion	Solvent $X^- / X^{2-}$	$e^+/e$	$e/e^-$	$e^-/e^+$	Reference
PcCr(II)	DMF/Py	+0.4/-0.155			tw
PcMn(II)	DMF/DMSO/Py	0.045/-0.10	-0.45/-0.575	-1.10/-1.28	3
PcFe(II)	DMF/DMSO/Py	0.90/-0.085	-0.31/-0.845	-0.87/-1.085	2
TsPcFe(II)	DMSO/KCN		-0.98	-1.31	4, 5
PcCo(II)	DCB/DMF/DMSO/Py/4-EtPy	0.88/0.24	-0.1/-0.7	-1.11/-1.18	tw, 8

c) Note: Supporting electrolytes include tetraalkylammonium chlorides, bromides, and perchlorates. Numbers indicate upper and lower boundaries for observed potentials. These data include tetrasulfonated and tetra-*t*-butyl derivatives. Solvents: DMF, dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; DCB, *o*-dichlorobenzene.

Table VI. Observed and Calculated Charge Transfer Data (DMF)

Complex	Observed Energy (cm <sup>-1</sup> )	Calculated Energy (cm <sup>-1</sup> )	Assignment <sup>a</sup>
TsPcCr(II)	11,780	11,935	LMCT1
	?	13,710	MLCT2
	25,510	24,925	LMCT2
TsPcCr(III)	7,900	8,870	LMCT1
	20,080	22,590	LMCT2
PcMn(II)	?	23,710	MLCT2
	10,910	10,970	LMCT1
	?	15,725	MLCT2
	26,300	26,180	LMCT2
TbPcMn(III)	7,630	6,535	LMCT1
	20,120	19,740	LMCT2
	?	22,100	MLCT2

<sup>a</sup> The charge transfer transitions concerned are  $a_{1u} \rightarrow e_g(d)$  LMCT1;  $a_{1u} \rightarrow e_g(d)$  LMCT2 and  $e_g(d) \rightarrow b_{1g}(\pi^*)$  MLCT2(31). The counterion for chromium(II) is a sulfonic acid residue, and for manganese(II) it is acetate.

Figure 1. A simplified energy level diagram for a metallophthalocyanine. LMCT and MLCT are ligand to metal, and metal to ligand charge transfer transitions, respectively.

Figure 2. Sketch of the variation in first-, second-, third-, and fourth-ring reduction potentials as a function of metal ion and oxidation state. All data vs. NHE.

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